

AD-A078 784

CORPS OF ENGINEERS BUFFALO N Y BUFFALO DISTRICT
CHEMICAL EXTRACTION AS AN INDEX OF BIOAVAILABILITY OF PHOSPHATE--ETC(U)
JAN 78 T J LOGAN

F/G 13/2

UNCLASSIFIED

| OF |
AD-
A078784

NL



END
DATE
FILED

1-80
DDC

ADA 078784

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE**READ INSTRUCTIONS
BEFORE COMPLETING FORM**

1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
6. TITLE (and Subtitle)		7. TYPE OF REPORT & PERIOD COVERED
Chemical Extraction As An Index of Bioavailability of Phosphate in Lake Erie Suspended Sediments		Final rep.
7. AUTHOR(s)		8. CONTRACT OR GRANT NUMBER(s)
P Terry J. Logan		NA
9. PERFORMING ORGANIZATION NAME AND ADDRESS		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
Agronomy Department - Ohio Agricultural Research and Development Center Wooster, OH 44691		34
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE
Water Quality Section NCBED-HQ U.S. Army Engineer District, Buffalo 1776 Niagara St., Buffalo, NY 14207		11 January 1978
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES
1255		52
16. DISTRIBUTION STATEMENT (of this Report)		15. SECURITY CLASS. (of this report)
		Unclassified
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
Approved for public release; distribution unlimited.		
18. SUPPLEMENTARY NOTES		
Copies are available from National Technical Information Service, Springfield, VA 22161		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
Lake Erie Drainage Basin Phosphorus		
Water Quality		
Chemical Extraction Procedures		
for "Sediment" Phosphorus		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		
The objectives of this report are:		
a. To characterize the phosphorus contained in suspended sediments from streams draining into Lake Erie.		
b. To study the differences in suspended sediment phosphorus entering Lake Erie in streams from different drainage basins.		
Yours		

CHEMICAL EXTRACTION AS AN INDEX OF
BIOAVAILABILITY OF PHOSPHATE
IN LAKE ERIE BASIN SUSPENDED SEDIMENTS

FINAL PROJECT REPORT
AGRONOMY DEPARTMENT
OHIO AGRICULTURAL RESEARCH AND DEVELOPMENT CENTER
WOOSTER, OHIO 44691

<u>Accession For</u>	
NTIS GRAAI	
DOC TAB	
Unannounced	
<u>Justification</u>	
<u>By</u>	
<u>Distribution/</u>	
<u>Availability Codes</u>	
Dist.	Avail and/or special
	<input checked="" type="checkbox"/>

Terry J. Logan
Project Leader

January 1978

LAKE ERIE WASTEWATER MANAGEMENT STUDY
U.S. ARMY CORPS OF ENGINEERS
BUFFALO DISTRICT, BUFFALO, N.Y.

DISTRIBUTION STATEMENT A

Approved for public release
Distribution Unlimited

TABLE OF CONTENTS

	<u>Page</u>
ACKNOWLEDGEMENTS	iii
INTRODUCTION	1
OBJECTIVES OF THE STUDY	13
METHODS	14
1. <u>Sample Collection</u>	14
2. <u>Handling and Storage of Samples</u>	15
3. <u>Analytical Methodology</u>	15
RESULTS AND DISCUSSION	26
1. <u>Bioavailable Sediment-P</u>	30
2. <u>Total Sediment-P Analysis</u>	34
3. <u>Extrapolation to Lake Erie</u>	35
CONCLUSIONS	37
REFERENCES	38
APPENDIX	42

ACKNOWLEDGEMENTS

The assistance of Dr. Steve Yaksich, LEWMS, Buffalo and Dr. David Baker, River Laboratory, Heidelberg College, Tiffin, Ohio, in obtaining samples is greatly appreciated. The work on this study is part of the Ph.D. dissertation of Mr. Tom Oloya, research associate, Agronomy Department, Ohio State University. This project was supported by a grant from the Lake Erie Wastewater Management Study, U.S. Army Corps of Engineers, Buffalo District, Buffalo, N.Y.

INTRODUCTION

The role of phosphorus in accelerated eutrophication of Lake Erie and other areas in the Great Lakes Drainage Basin has been recognized and documented in recent years. Studies by LEWMS and PLUARG have shown that a major part of the total phosphorus load entering the lakes from tributary drainage is in the form of particulate-P. While it is readily accepted that soluble inorganic-P in drainage water is available to algae and other aquatic vegetation, the bioavailability of sediment-bound phosphate is largely unknown. As a result, one is faced with two extreme scenarios: a) only the soluble inorganic-P is bioavailable and b) all sources of P including sediment-P are available. The first scenario is supported by the findings in New York where soluble inorganic-P was shown to be the dominant form of stream-transported phosphate in stimulating growth of algae (Porter, 1975). On the other hand, Golterman (1977) found that sediment-P in shallow polder lakes in Holland would maintain highly eutrophic conditions even if all external P sources were removed. Recent work by Allan and Williams (1978) demonstrated the importance of biologically available sediment-P in fairly shallow Canadian prairie lakes.

The importance of sediment as a source of P for algae is governed by a number of factors. Streams which carry a low sediment load, and/or sediment of coarse-texture and stream-bank origin will have most of its biologically available P as soluble inorganic-P as a consequence of the lower P content of coarse sediment (Williams *et al.*, 1976). Consideration must also be given to physical lake dynamics. Stream sediments which settle rapidly into deep lakes will only be positionally

available to algae in the photic zone for short periods as in the central and eastern basins of Lake Erie, thereby minimizing the significance of sediment-P as a source of biologically available phosphorus. In contrast, we have the situation where streams carry a high load of fine-grained sediment into shallow lakes, a situation similar to that in the western basin of Lake Erie. In this instance, factors which serve to increase the importance of sediment-P are: the high percentage of the total phosphorus load as sediment-P, the higher content of P in clay-sized sediment, and the longer period in which this suspended sediment load is positionally available to algae in the photic zone.

Chemical extraction procedures to estimate bioavailability of sediment-P from tributary sources must take into account the conditions under which algae obtain P from sediment. Algae can derive some P from sediment in the photic zone for short periods and under aerobic conditions. In addition, available-P is derived from bottom sediments during anoxic regeneration and subsequent lake inversion, a markedly different chemical environment than exists in the photic zone. While much of the P regeneration is from decomposed algal biomass, sediment-P is also released under anoxic conditions. As a result of this dichotomy, bioavailable sediment-P will be viewed here in two ways: a) positionally available, to represent short-term release of P to algae in surface waters, and b) total potentially available, to represent maximum P which can be released over time by all mechanisms. Chemical extraction procedures to estimate sediment-P bioavailability will be discussed in the context of this concept.

In the following sections, discussion will include:

- 1) Differences in characteristics of soils, suspended sediments and bottom sediments
- 2) Chemical extraction procedures to estimate sediment bioavailability and their relation to sediment properties
- 3) Estimates of phosphorus bioavailability of Lake Erie sediments
- 4) Kinetics of desorption and chemical exchange of sediment-P.

1. Some contrasting characteristics of soils and sediments

There is a growing body of research on chemical extraction procedures to estimate bioavailable sediment-P (BSP). Much of the early work was done on soils, with more recent studies on lake and stream sediments. Differences in these studies can be attributed, in part, to differences in the biological and physicochemical characteristics of soils and sediments. A major treatment of the subject is not intended here. However, several major differences between soils and sediments are apparent. First, because of their fluvial transport, sediments are unstructured and generally more fine-grained than the soils from which they were derived. They tend to be enriched in organic matter, and this together with their fine-grained nature results in an enrichment of sediments with phosphate, hydrous oxides of iron and some aluminum, and, in some sediments with carbonates. Suspended stream sediments behave much like their soil precursors except for their P enrichment (Green *et al.*,

1978). Bottom sediments, on the other hand, in both lakes and streams may be subjected to long periods of anoxia with subsequent reduction and solubilization of iron (Patrick and Mahapatra, 1968). Phosphate release from suspended sediments is much more similar to that from soil than from bottom sediments. Discussion of chemical extraction of sediment-P must consider these significant differences.

2. Chemical extraction procedures to estimate BSP

Any chemical extraction procedure to estimate soil or sediment bioavailability must have the following attributes:

1. Must correlate with biouptake
2. Should be applicable to a wide range of soils or sediments
3. Should be relatively easy to perform and the results should be reproducible.

Early work in soil science was concerned with development of soil test procedures, i.e. chemical extractants to estimate availability of soil-P to agronomic crops. Most of the procedures did one or more of the following:

1. Removed soluble-P held in soil pores
2. Used another anion to exchange with some of the $H_2PO_4^-$ adsorbed to soil surfaces
3. Dissolved or hydrolyzed part of the more labile soil-P complex.

Many of the procedures used, in fact, do all three. In the Lake Erie Basin, today, two soil testing procedures for plant-available phosphate

are used: 0.5 M NaHCO₃ (Olsen et al., 1954) and the Bray P1 (0.03 M NH₄F + 0.025 M HCl) (Bray and Kurtz, 1945). The Bray procedure is used in all the U.S. Lake Erie Basin states and the Olsen test in Ontario. These tests have also been used to characterize sediment-P (Romkens and Nelson, 1974; McCallister and Logan, 1978).

Workers at Wisconsin (Chang and Jackson, 1957) began to look at sequential chemical extraction to characterize soil-P. Their original theory was that phosphorus in soil occurred as discrete chemical forms which could be selectively removed by sequential chemical extraction. They proposed the following scheme:

<u>Chemical form</u>	<u>Extractant (in sequence)</u>
Salloid-bound P	1 <u>N</u> NH ₄ Cl
Aluminum-P	0.5 <u>M</u> NH ₄ F
Iron-P	1 <u>N</u> NaOH
Occluded-P	citrate-dithionite-bicarbonate
Apatite-P	1 <u>N</u> HCl

This theory of discrete P forms in soil has been questioned by Bache (1963, 1964), Bauwin and Tyner (1957) and others. A more prevalent view today is that much of the inorganic-P in soil is chemisorbed to a number of reactive surfaces including iron and aluminum oxides and hydrous oxides, amorphous aluminosilicates and carbonates, or occluded in the matrices of a number of soil mineral forms. Probably only small amounts of apatite in some soils are representative of the discrete P form envisaged by Chang and Jackson (1957). Nevertheless, their scheme for chemical fractionation of soil-P proved to be highly useful in looking at relative differences between soils, and their work proved to be the

stimulus for much subsequent research in this area (Logan and McLean, 1973; Fiskell and Spencer, 1964; Robertson *et al.*, 1966).

While the original fractionation schemes were designed to study the effects of soil genesis on soil-P forms, it was quickly adopted by soil chemists as a tool for the study of phosphorus fertilizer reactions in soil, and, more recently, as an indicator of soil potential for water pollution (Reddy *et al.*, 1978). The utility of these schemes is based not on their ability to extract discrete P forms, but because the scheme uses sequential extraction, and because the order of the sequence is from least severe and most selective to most severe and least selective. If one accepts the fact that P is bound to many different surfaces in soil with varying binding forces, and that the P which is held on the weakest sites will be the most environmentally reactive, then this type of sequential extraction, in effect, partitions soil and sediment phosphate on the basis of binding strength.

Major developments in the basic scheme proposed by Chang and Jackson (1957) have been accomplished by Williams and Walker (1969a and b); Williams *et al.* (1967); Williams *et al.* (1971a and b); Allan and Williams (1978) for soils and lake sediments. Syers *et al.* (1972) encountered problems with the NH_4F extractant for aluminum-P and dropped it in favor of NaOH as a single extractant for the combined iron- and aluminum-bound P fractions. Most workers have also dropped the NH_4Cl extraction because the amount of P extracted is very low compared to other fractions. More recently, Williams (Williams *et al.*, 1976; Allan and Williams, 1978) has simplified the scheme for lake sediments even further. He proposes two inorganic sediment-P fractions: nonapatite phosphorus (NAIP) extracted

by citrate-dithionite-bicarbonate (CDB), and apatite-P extracted by HCl or H_2SO_4 . Allan and Williams (1978) have proposed that the NaIP fraction be considered bioavailable, based on correlations of CDB extraction with the NTA extraction of Golterman (1976) which was found to estimate sediment-P availability to Scenedesmus.

Few studies are available which give direct correlation between algal P uptake from sediment and chemical extraction. The work of Golterman (1976) has already been mentioned. Sagher et al., (1975) found that 0.1 N NaOH extractable P was highly correlated with P uptake by P-deficient algae when sediment-P was the only phosphate source. More recently, Corey (personal communication) used the same algal assay system as Sagher et al., (1975) and found high correlation of algal extractable P with sediment-P extracted by aluminum-saturated exchange resin. Cowen and Lee (1976) found that amounts of P available in New York urban runoff sediment to Selenastrum were similar to that extracted by anion exchange. Correlation with anion exchange extraction was better than with 0.1 N NaOH extraction, the base extraction significantly overestimating bioavailability. Their data will be discussed further in another section.

Another method for estimating BSP involves the thermodynamic response of sediment surfaces to reactive inorganic phosphate. Figure 1 gives an idealized isotherm for adsorption-desorption of inorganic P by soil or sediment.

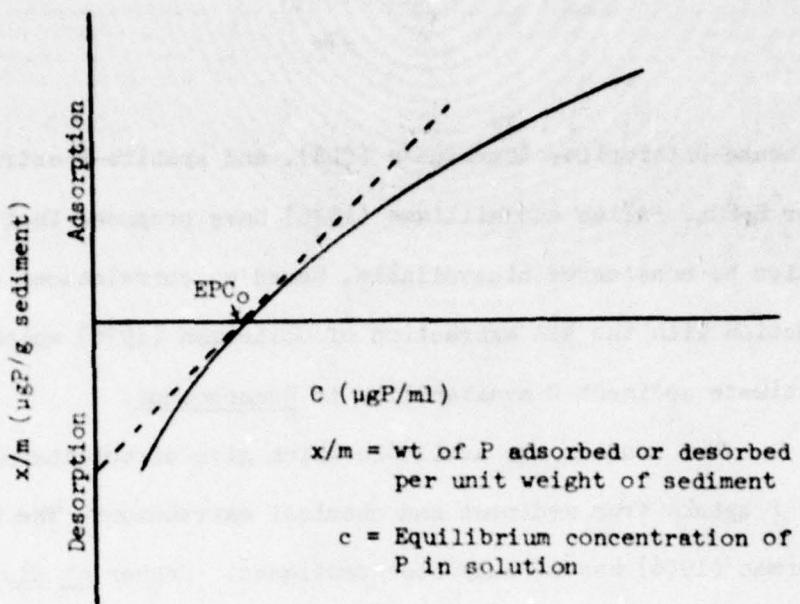


Figure 1. Adsorption/desorption curve (idealized) for soil or sediment.

Net adsorption occurs when equilibrium P concentration exceeds EPC_0 , and net desorption when $C < EPC_0$. EPC_0 , the equilibrium P concentration at which P is neither adsorbed nor desorbed is a useful parameter for predicting soluble inorganic P concentrations in equilibrium with suspended sediment (Taylor and Kunishi, 1971; McCallister and Logan, 1978; Green *et al.*, 1978; Ryden *et al.*, 1972). Of equal importance, however, is the buffer capacity of the sediment, i.e. the amount of P that must be adsorbed or desorbed by unit mass of sediment to produce a unit change in soluble inorganic P concentration. Taylor and Kunishi (1971) define BSP as the amount of P that must be desorbed by sediment to reduce equilibrium P concentration from EPC_0 down to some arbitrary value at which P is limiting to algae growth. This value can be obtained as the slope of

the curve in Figure 1 (dotted line). Sediment buffer capacity is a function of such factors as surface area (related to clay content of sediment), reactive surfaces on sediment particle and amount of labile P already adsorbed. Bouldin used a similar procedure to estimate BSP for tributary drainage into New York lakes (Porter, 1975). Procedures of this kind usually involve short-term incubation (< 6 days) and probably represent the most biologically available sediment-P, but, at the same time, probably underestimates total potential BSP.

3. Kinetics of exchange and desorption of sediment-P

Procedures discussed previously in this report deal with the capacity of sediment to supply inorganic P to organisms. Little work has been done, however, on the rate of release of sediment-P. Isotopic exchange rates using ^{32}P were measured in soils (Amer et al., 1955) and sediments (Li et al., 1972). They showed that exchange involved at least three different reactions, the fastest coming to completion in 15 minutes and the slowest continuing for at least 72 hours. Both studies showed that a large percentage of the exchangeable P was exchanged during the initial rapid reaction. Rajan and Fox (1975) demonstrated that P adsorption by soil showed a fast and slow reaction, and that desorption of P occurred at a rate similar to the slow adsorption reaction. Ryden et al. (1977) have attributed the fast exchange reaction to a physical adsorption of H_2PO_4^- anions by positively charged colloid surfaces, while the slow reaction may involve precipitation-dissolution of metal-phosphate complexes and diffusion of phosphate ions from chemically bound sites to more labile positions. After desorption

of the physically sorbed labile P, the slow desorption of phosphate may determine the rate at which algae can obtain inorganic P from sediment.

Almost all desorption studies (Ryden *et al.*, 1972; McCallister and Logan, 1978; Green *et al.*, 1978) have involved batch equilibration of soil or sediment with P-free distilled water or dilute electrolyte. While this information is useful in characterizing relative ability of sediments to supply P, they shed little light on the kinetics of P release in the presence of a continuous sink, i.e. algae.

4. Estimates of bioavailability of sediment-P in Lake Erie Basin suspended sediments and other sediments

Interest in sediment-P bioavailability has increased in the last decade as research into the causes of cultural eutrophication in lakes has increased. Since 1970, a number of studies, using the many different procedures discussed previously, have been used to estimate RSP. This is usually expressed as ugP/g sediment or as a percentage of the total sediment-P or total inorganic-P. In this section, some of the results will be compared, and wherever possible, common units will be used.

Sagher *et al.*, (1975) studied algal uptake of sediment-P from several Wisconsin lakes and correlated uptake with chemical extraction. Highest correlation was obtained with 0.1 N NaOH extraction. They found that > 80% of total sediment inorganic-P was available to algae for noncalcareous sediments. Williams *et al.*, (1971b) had shown previously that NaOH-P would extract most of the inorganic-P in noncalcareous Wisconsin lake sediments. In calcareous sediments, 50-70% of the sediment inorganic-P was found to be bioavailable (Sagher *et al.*, 1975).

Cowen and Lee (1976) studied P bioavailability of urban runoff and stream sediments in Wisconsin and New York, using algal incubation techniques as well as chemical and resin extraction. Madison, Wisconsin urban runoff sediment gave BSP values of ~ 30% of total P as measured by either incubation with Selenastrum, resin extraction or NaOH extraction, with a range of 2-55% depending on individual sample or method used. Resin extraction gave somewhat lower values than either Selenastrum bioassay or base extraction.

In New York urban runoff sediments, resin and base extraction gave similar results, 16 and 22% of total sediment-P, respectively, with a range of 1-37% depending on individual sample and method employed. Selenastrum bioassay, however, was < 9%. Genesee River sediments gave a value of 6% with Selenastrum bioassay, while resin extraction gave 6 to 31%. The authors attributed the lower bioassay value to competition for P by native algal species in the sample during incubation. One must conclude from their work that while resin or base extraction gives reasonable estimates of BSP for Wisconsin sediments, these procedures will overestimate BSP for New York sediments.

Recently, Nelson (1978) studied BSP of suspended sediments in the Black Creek watershed in Indiana. This 5000 hectare watershed is located in the western Maumee River Basin, and is typical of much of the rural land use and geochemistry of western Ohio and north-eastern Indiana. They used Selenastrum bioassay and sequential chemical extraction to estimate BSP. Their chemical extraction procedure included 0.5 M NH₄F prior to 0.1 M NaOH, and as such, represents the original scheme developed by Chang and Jackson (1957). It is the opinion of this author based on

unpublished work in our laboratory that a substantial portion of the NH_4F -extractable P would be extracted by NaOH alone. The sum of these two fractions accounted for between 71 and 87% of the sediment inorganic P extracted by Selenastrum. This represented between 19 and 29% of the total sediment inorganic P. Nelson (1978) also found that sediments from agricultural drainage areas had lower BSP than from an agricultural area influenced by P input from a small village. The Maumee River at the outlet of Black Creek was somewhat higher in BSP than the other areas.

While it has been recognized (Williams et al., 1976) that fine-grained sediments are often higher in total P and organic matter than coarser sediments, little data is available on P bioavailability of different sized sediment fractions. Armstrong et al. (1977) have reported on preliminary results of chemical extraction of sediment-P for different sized sediment fractions in Great Lakes tributaries (Genesee R., New York; Maumee R., Ohio; Grand R., Michigan; Menomonee R., Wisconsin; Nemadji R., Minnesota). Maumee and Nemadji sediments were highest in total clay, the Genesee highest in silt (2-20 μ) and the Menomonee had the highest percentage in the size range $> 20 \mu$. In most cases, total-P and resin extractable-P or NaOH extractable-P as percent of total P increased as particle size decreased. In all size ranges, Maumee sediment had the highest bioavailability (as estimated by either resin or NaOH extraction) and the Nemadji the lowest. Genesee and Menomonee sediments were intermediate and similar. BSP (as percent of total sediment-P) ranged from 5-48%.

OBJECTIVES OF THE STUDY

1. To characterize the phosphorus contained in suspended sediments from streams draining into Lake Erie.
2. To study the differences in suspended sediment phosphorus entering Lake Erie in streams from different drainage basins.
3. To estimate the bioavailability of phosphorus to aquatic plants from suspended sediments in streams draining into Lake Erie.

METHODS

1. Sample Collection

During the period March through July, 1977, a total of 66 samples were collected from 36 tributary locations in the Lake Erie drainage basin on the U.S. side. A summary of the sites, tributaries, sampling dates, etc. are given in Table 1. Six major tributaries in Michigan and two smaller streams with drainage areas ranging from 20 to 1042 mi² (52-2698 km²) were sampled between March 5 and May 16. In Ohio, eight major tributaries and ten smaller streams ranging in drainage area from 0.3 to 6330 mi² (0.8-16395 km²) were sampled between March 10 and July 7. In New York four creeks ranging from 10 to 37 mi² (26-96 km²) were sampled on April 23.

The sites were arbitrarily separated into four groups:

1. Michigan streams
2. Maumee-Portage-Sandusky-Huron river basins
3. Eastern Ohio streams
4. New York streams

This division allows some separation on the basis of land use and geochemistry.

Samples provided were either part of an ongoing monitoring program or were taken for this study. Some samples were pumped while others were grab sampled. Drs. Steve Yaksich, U.S. Army Corps of Engineers Buffalo District and David Baker, River Laboratory, Heidelberg College, Tiffin, Ohio provided most of the samples. Most samples were taken during the period of medium to high flow (Table 1) and so represent the period of maximum sediment transport.

Sample sites are located in Figure 2 by numbers which correspond to those in Table 1.

2. Handling and Storage of Samples

A four-liter sample of sediment suspension was collected.

Upon delivery, each sample was vigorously shaken to disperse the sediment and two 250-ml aliquots were taken (Figure 3). One 250-ml aliquot was filtered through a 1.0 μm Nucleopore filter and the filtrate stored in polyethylene bottles and frozen. The second 250-ml aliquot was left unfiltered and stored at 4°C in polyethylene bottles. The remaining 3.5 liters was allowed to stand overnight at 4°C for sediment to settle.

After settling, the supernatant was siphoned out into another container. The sediment was shaken and transferred to a smaller container and left to settle. After most of the supernatant was poured out, the sediment was freeze-dried and stored.

The supernatant was centrifuged and filtered to recover any of the finer sediment that did not settle. This was added to the sediment.

3. Analytical Methodology

A 20-ml aliquot of the filtered sample was analyzed for filtered* reactive phosphorus (FRP) by the method of Murphy and Riley (1962) as modified by John (1970). The following changes were made in

* This is equivalent to dissolved inorganic-P (DIP). However, DIP is defined as having been filtered through 0.45 μm filter and we used 1.0 μm . Our studies indicate no significant differences with the two methods.

Figure 2. Lake Erie Drainage Basin tributary sampling sites.

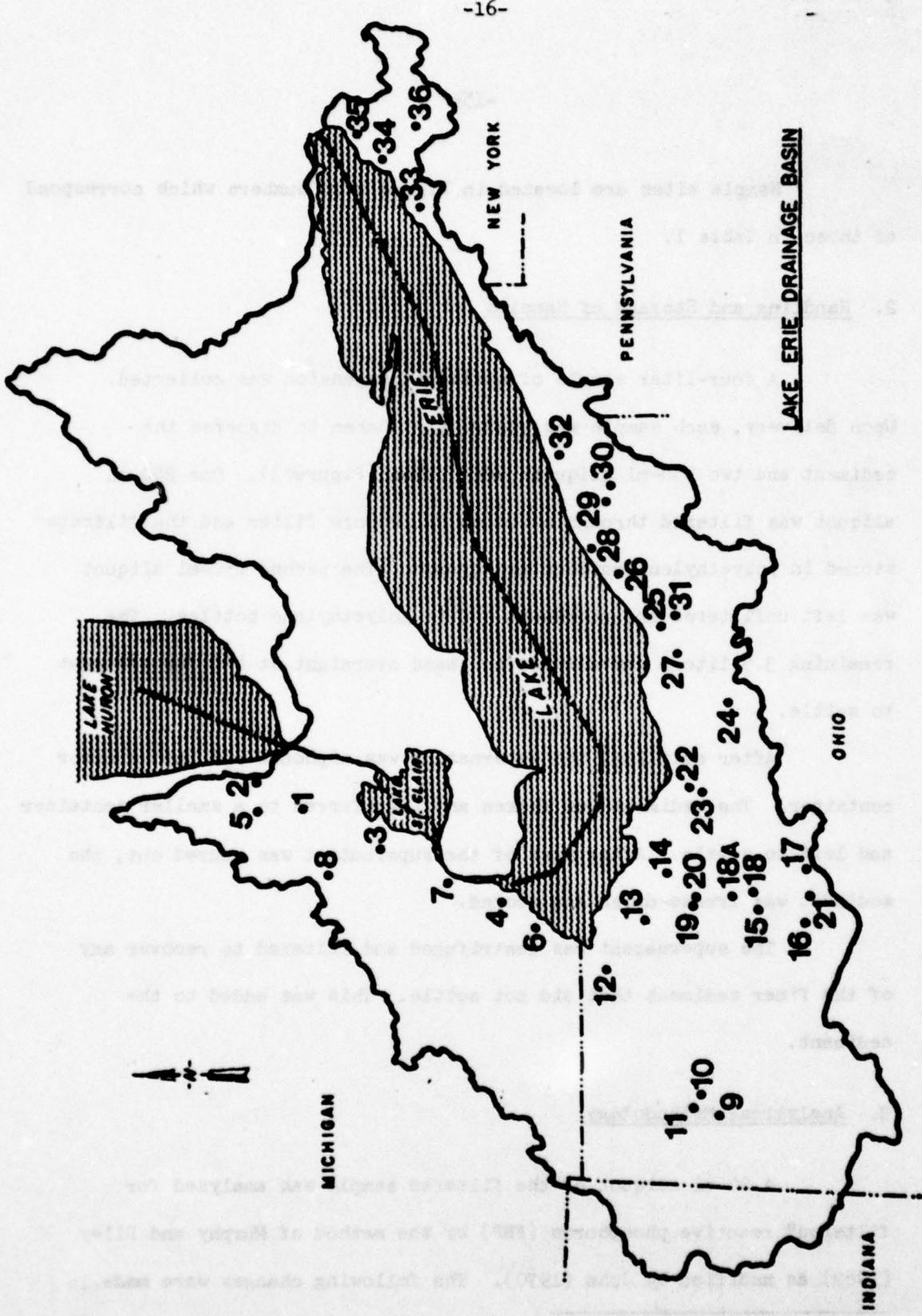


TABLE 1. CHARACTERISTICS OF LAKE ERIE THERMOTRANSMITTER SAMPLES 67700 (1977)

Map No.	Station No.	Stream	Sampling Site	County	Latitude	Longitude	Sampling Date	Sample No.	Mean Annual Discharge ft ³ /sec	Mean Discharge of Month Sampled ft ³ /sec	Mean Discharge of Year Sampled ft ³ /sec
Metroparks											
1	04150000	Belle	Sample	St. Clair	42°1.09	82°1.39	1, 9	69.0	172, 21	52,934	13
2	04159000	Black	Forge	St. Clair	42°1.2	82°1.39	2, 10	282.0	692, 43	1120, 948	41
3	04159200	Clemon	St. Clair	Monroe	40°1.06	82°1.39	3, 11	394.0	1384, 322	2462, 2448	219
4	04159300	Metropolitan Hwy.	Area	St. Clair	42°1.72	82°1.39	4, 12	520.0	303, 266	303, 266	-17-
5	04159300	Mill Creek	Monroe	St. Clair	42°1.71	82°1.39	5, 13	92.0	1277, 367	1277, 367	377
6	04170000	Red	Monroe	St. Clair	40°0.70	82°1.39	6, 14	698.0	2780, 3200	2780, 3200	
7	04170200	West Jefferson Bridge	Wayne	St. Clair	40°0.53	82°1.39	7, 15	22.0	116, 171	116, 171	
8	04180000	Wadsworth Creek	Sample	Clinton	41°1.13	82°1.39	8, 16	12.5	22, 6.6	21, 7.1	
Metroparks-Portage-Sandusky-Ashtabula											
9	04180000	Ashtabula	Portage	Ohio	40°10. 4/26	82°1.38	1702	2916, 2693			
10	04180000	Independence	Portage	Ohio	40°10. 7/1	82°1.38	26, 41				
11	04181000	Portage	Portage	Portage	39°06	82°1.0	27				
12	04193000	Monroe	Waterville	Lucas	40°36. 7	82°1.35	28, 39	4797.0	13680, 11900	26820, 22900	1110
13	04193000	Portage	Woodville	Sandusky	41°06. 52	82°1.35	33, 50	304.0	1165, 171	1540, 511	
14	04193000	Portage	Woodville	Sandusky	40°46. 09	82°28. 7/2	34, 47	948.0	2162, 539	1760	
					7/3					2180, 2220	

TABLE 1. (Continued)

Map No.	Station No.	Stream	Sampling Site	County	Drainage Area sq. mi.	Sampling Date	Sample No.	Mean Annual Discharge ft./sec.	Mean Discharge of Month sampled ft./sec.	Mean Discharge of Date Sampled ft./sec.	Mean Discharge of Date Sampled ft./sec.
15	04397000	Sainteely	Marie	Seneca	2004.66	3/26	32	575.0	1401	1153	1153
16	04395000	Sainteely	Upper Sainteely	Wyandot	771.82	3/26	35	241.0	467	295	148
17	04396000	Sainteely	Bogus	Crawford	229.99	3/25	32	64.6	121	142	142
18	04397100	Hominy Creek	Hominy	Seneca	365.91	3/21, 3/28 4/5, 7/1	29, 31 37, 42	200	54	323	15
19a		Willow Creek	Willow	Seneca	771	14					
19	04397300	Wolf Creek	Betterville	Seneca	171.46	7/1	45	42	10.2	127	127
20	04397150	Wolf Creek	West Branch	Seneca	213.42	3/26	36	100	497	1650	1650
21	04396200	Wolf Creek	East Branch	Wyandot	217.04	7/1	43	70	51	724	724
22	04399000	Barren	Willam	Erie	260.86	7/5	43	293	716	253	253
23	04396200	Barren Creek	Barren	Seneca	12.76	6/6	30	14.37	7123	7123	7123

Table 1. (Continued)

Top No.	Station No.	Stream	Sampling Site	County	Drainage Area sq. mi.	Sampling Date	Sample No.	Mean Annual Discharge ft. ³ /sec.	Mean Discharge at Month Sampled ft. ³ /sec.	Mean Discharge of Nine Samples ft. ³ /sec.
Eastern Ohio										
26	0420900	Jeff Run	Jeffersfield	Medina	1.97	6/6	57	2.0		
27	0420900	Big Creek	Cleveland	Cuyahoga	91.53	6/6	53	53.4	55.7	71.0
28	0420900	Chagrin	Village City	Lake	637.18	6/6	54	326	349	365
27	0420900	Randy	Reyes	Cuyahoga	691.53	6/6	60	260	28.9	11.0
28	04212100	Grand	Palmerville	Clark	1778.15	6/6	59	934	72.4	-19-
29	0421000	Nestville Branch	Nestville	Cuyahoga	0.75	6/6	59	28		
30	0420100	Robins Creek	Independence	Autauga	16.08	6/6	56			1.50
31	0420800	Cuyahoga	Independence	Cuyahoga	1831.13	6/6	55	769	342	300
32	0422500	Robert Run	Autauga	Autauga	2.26	7/7	62			0.73
Erie, York										
33	04213500	Casselman Creek	Greene	Erie	1118.88	3/28	62		2274	2250
34	04214640	Delaware Creek	Angola	Erie	12.95	4/23	62		1478	1470
35	04215200	18 Mile Creek	S. Benton	Erie	56.35	4/23	64		303	303
36	04213600	S. Casselman	Ohio	Casselman	66.30	4/23	66		300	300
									1100	1100

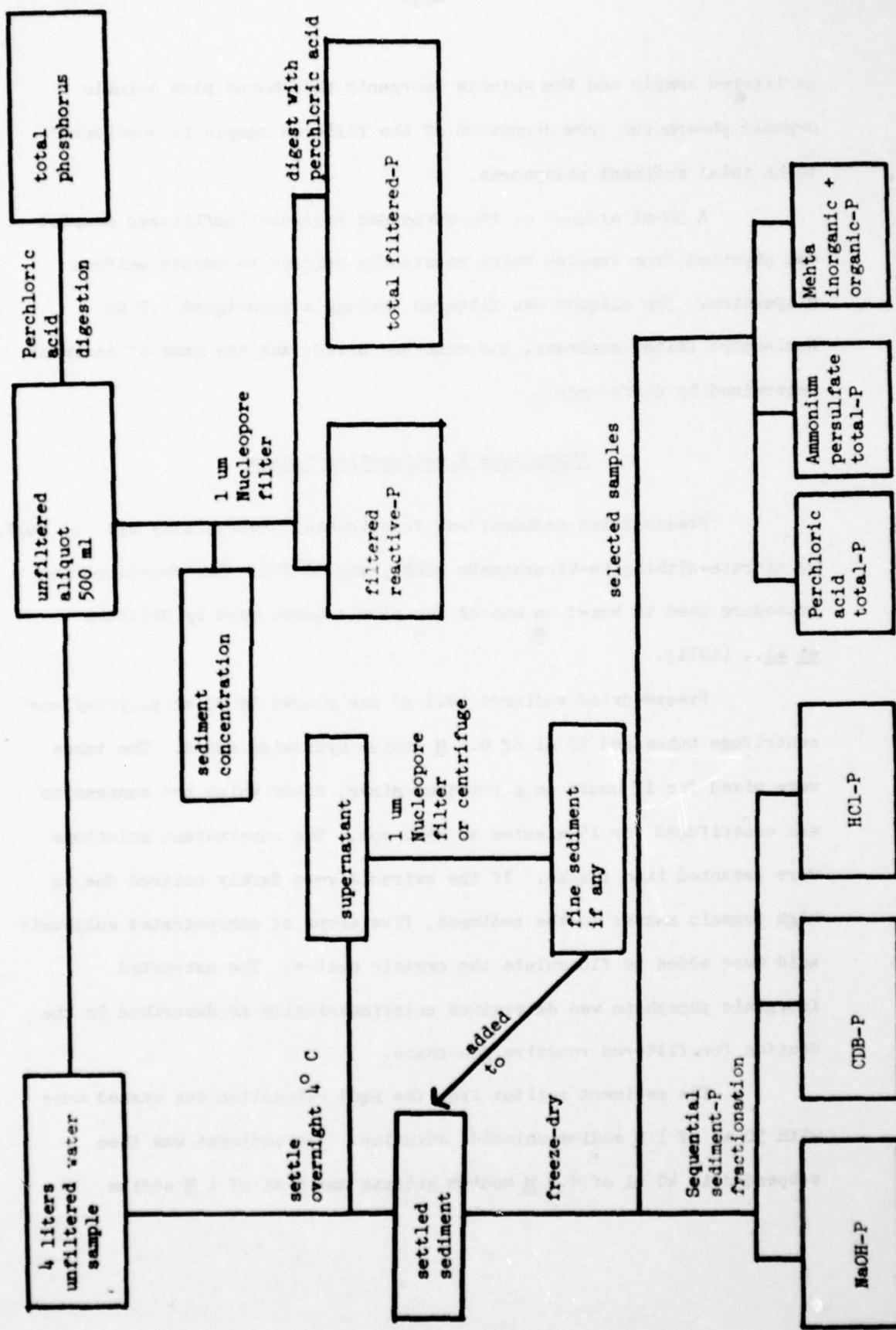
order to improve the stability of the blue molybdo-phosphate complex.

Absorbance readings were taken with a Beckman 24 Spectrophotometer at 730 nm wavelength and inorganic P concentrations determined from a standard curve.

Total phosphorus was determined by the method of Sommers and Nelson (1972). Twenty-ml aliquots of the unfiltered samples were pipetted into 50-ml digestion tubes. Five drops of concentrated sulphuric acid were added to the suspension and the samples evaporated in an oven at 105°C overnight. On cooling, 3 ml of 70% perchloric acid were added, and pyrex funnels were placed atop the tubes throughout the digestion to ensure refluxing of perchloric acid. The tubes were placed in an aluminum digestion block and the samples digested at 203°C for 75 minutes. Following digestion, the digest was allowed to cool, and then diluted with distilled water to 50 ml. The tubes were shaken to mix the contents and left to stand overnight or centrifuged to remove residues. From the clear supernatant solution 10 ml aliquots were pipetted into 50 ml tubes, neutralized with 5 N NaOH using p-nitrophenol as an indicator. The aliquot was analyzed for total phosphorus colorimetrically as described in the section for filtered reactive phosphorus.

Twenty-ml aliquots of the filtered samples were digested in 70% perchloric acid following the procedure outlined for total phosphorus digestion. The phosphorus from this digestion is the sum of soluble inorganic and soluble organic phosphorus. The difference between the values obtained from the digestion of the filtered samples and the soluble inorganic phosphorus is considered to be soluble organic phosphorus. The difference between total phosphorus obtained from digestion of the

Figure 3. Sample handling and analysis



unfiltered sample and the soluble inorganic phosphorus plus soluble organic phosphorus from digestion of the filtered sample is considered to be total sediment phosphorus.

A 50-ml aliquot of the suspended sediment (unfiltered sample) was pipetted from samples being constantly stirred to ensure uniform dispersion. The aliquot was filtered through a preweighed 1.0 μ m Nucleopore filter membrane, the membrane dried, and the mass of sediment determined by difference.

Phosphorus Fractionation Scheme

Freeze-dried sediment was fractionated sequentially by: 1) NaOH, 2) citrate-dithionite-bicarbonate (CDB), and 3) HCl. The fractionation procedure used is based on one of the five schemes used by Williams *et al.*, (1971).

Freeze-dried sediment (0.1 g) was placed in 90-ml polyethylene centrifuge tubes and 50 ml of 0.1 M sodium hydroxide added. The tubes were mixed for 17 hours on a rotating mixer, after which the suspension was centrifuged for 15 minutes at 2400 rpm. The supernatant solutions were decanted into flasks. If the extracts were darkly colored due to high organic matter in the sediment, five drops of concentrated sulphuric acid were added to flocculate the organic matter. The extracted inorganic phosphate was determined colorimetrically as described in the section for filtered reactive phosphate.

The sediment residue from the NaOH extraction was washed once with 50 ml of 1 M sodium chloride solution. The sediment was then suspended in 40 ml of 0.3 M sodium citrate and 5 ml of 1 M sodium

bicarbonate, and then 1.0 gm of sodium dithionite was added. The suspension was heated in a water bath at 80-85°C for 15 minutes with frequent stirring. The suspension was cooled and mixed for 5 minutes on a rotating mixer, and then centrifuged for 10 minutes at 2000 rpm. The supernatant solution was decanted.

In the determination of inorganic-P after citrate-bicarbonate-dithionite extraction, there are interferences from dithionite, citrate, iron and silicon. Therefore, a simplified and more rapid procedure for the determination of reductant-soluble phosphate by a modification of Murphy and Riley (1962) ascorbic acid developed by Weaver (1974) was used. Excess sodium dithionite in the extract was oxidized by bubbling moist air through the extract over-night; 5 ml aliquots were pipetted from the air-oxidized extract into tubes, and 3 ml of 5% ammonium molybdate solution added. Addition of the 5% ammonium molybdate solution compensates for the interference from citrate. Distilled water was added to make approximately 40 ml volume and the "mixed reagent" for color development added and absorbance measured at 730 nm after 30 minutes. The blank was made by mixing 25 ml of 0.3 M sodium citrate, 1 gm of sodium dithionite, and the mixture diluted to 50 ml. This solution was oxidized in the same manner for same period of time, and 5 ml aliquot pipetted into a 50 ml tube.

The sediment residue from the CDB extraction was washed once with 1 M sodium chloride solution; 50 ml of 1 N hydrochloric acid was added and the suspension mixed in a rotating mixer for one hour. The suspension was centrifuged and the supernatant decanted; 20 ml aliquot of the extracts were pipetted into 50 ml tubes, neutralized with

5 N sodium hydroxide and the phosphate determined colorimetrically as for filtered reactive phosphorus. The residue after HCl extraction was digested with perchloric acid as before and is termed residual inorganic-P.

Total Phosphorus in Sediment

Total phosphorus on sediment was determined by the following three methods:

1. Perchloric acid
2. Persulphate
3. Mehta

Perchloric acid method: Total phosphorus of the sediment was determined by the method of Sommers and Nelson (1972). A 0.1-gm sample of the freeze-dried sediment was placed in a digestion tube and digested in 3 ml of perchloric acid at 203° for 75 minutes. Following digestion, the digest was allowed to cool and diluted with distilled water to 50 ml. The tubes were shaken and left to stand overnight or centrifuged to remove residues. From the clear supernatant solution, 3-ml aliquots were pipetted into 50 ml tubes, neutralized with 5 N NaOH using p-nitrophenol as an indicator. The aliquot was analyzed for total phosphorus colorimetrically as described in the section for FRP.

Mehta method: Total phosphorus in sediment was determined by the method of Mehta (1954). The method was modified slightly in the quantity of extracting reagents in proportion to the amount of sediment analyzed. A 0.1 gm sample of freeze-dried sediment was placed in digestion tube, and 5 ml of concentrated hydrochloric acid added, and then heated for 10 minutes at 70°C. An additional 5 ml of concentrated hydrochloric

acid was added, mixed and allowed to stand for one hour. Ten milliliters of distilled water was added, mixed, and then centrifuged. The clear supernatant solution was poured into a 50-ml tube, 10 ml of 0.5 N sodium hydroxide was added to the residue, stirred and the suspension allowed to stand at room temperature for one hour, after which it was centrifuged. The supernatant solution was poured into the tube containing the concentrated hydrochloric acid extract. Twenty milliliters of 0.5 N sodium hydroxide was added to the residue, stirred and covered with an inverted 50 ml beaker, and warmed in the oven at 90°C for 8 hours. The tube was cooled, centrifuged and the supernatant poured into the tube of HCl and NaOH extracts. The volume was made to 50 ml and mixed. Two 10-ml aliquots of the mixed extract were placed in two separate tubes. The first aliquot was analyzed for total inorganic phosphorus colorimetrically as described for FRP. The second aliquot was digested with perchloric acid as described previously, then analyzed for inorganic-P. The difference between the digested and nondigested aliquots is organic-P.

Persulphate method: Total phosphorus in sediments was determined by the persulphate method described in the Standard Methods for the Examination of Water and Wastewater (1975). The procedure was modified for the analysis of 0.05 gm of sediment suspended in water. A 0.05-gm sample of sediment was placed in a 100-ml volumetric flask and about 60 ml of distilled water added; 1 ml of sulphuric acid solution and 15 ml of potassium persulphate solution were added and the mixture heated for 30 minutes in an autoclave or pressure cooker at 15-20 psi. The mixture was then cooled, made to 100 ml, and an aliquot taken, neutralized with NaOH and phosphorus determined by the procedure described previously for FRP.

RESULTS AND DISCUSSION

The data was organized into the four geographical areas discussed previously. The complete data set is given in Appendix A for all parameters measured. Summary statistics by area are given in Table 2, and mean and S.D. are presented graphically in Figure 4. Sediment concentrations were significantly higher in the New York samples, with the western Ohio samples intermediate. Filtered reactive-P was highest in the eastern Ohio streams although the variation was quite high. Total P reflected both the high sediment concentrations in New York streams and high FRP in the eastern Ohio streams. Total sediment-P is calculated as the difference between total and total filtered-P divided by sediment concentration. Our data show that these values are overestimated at low sediment concentrations (Appendix A) when compared with direct measurement of total P on sediment. Errors in the three parameters which are used to calculate total sediment-P may contribute to this difference.

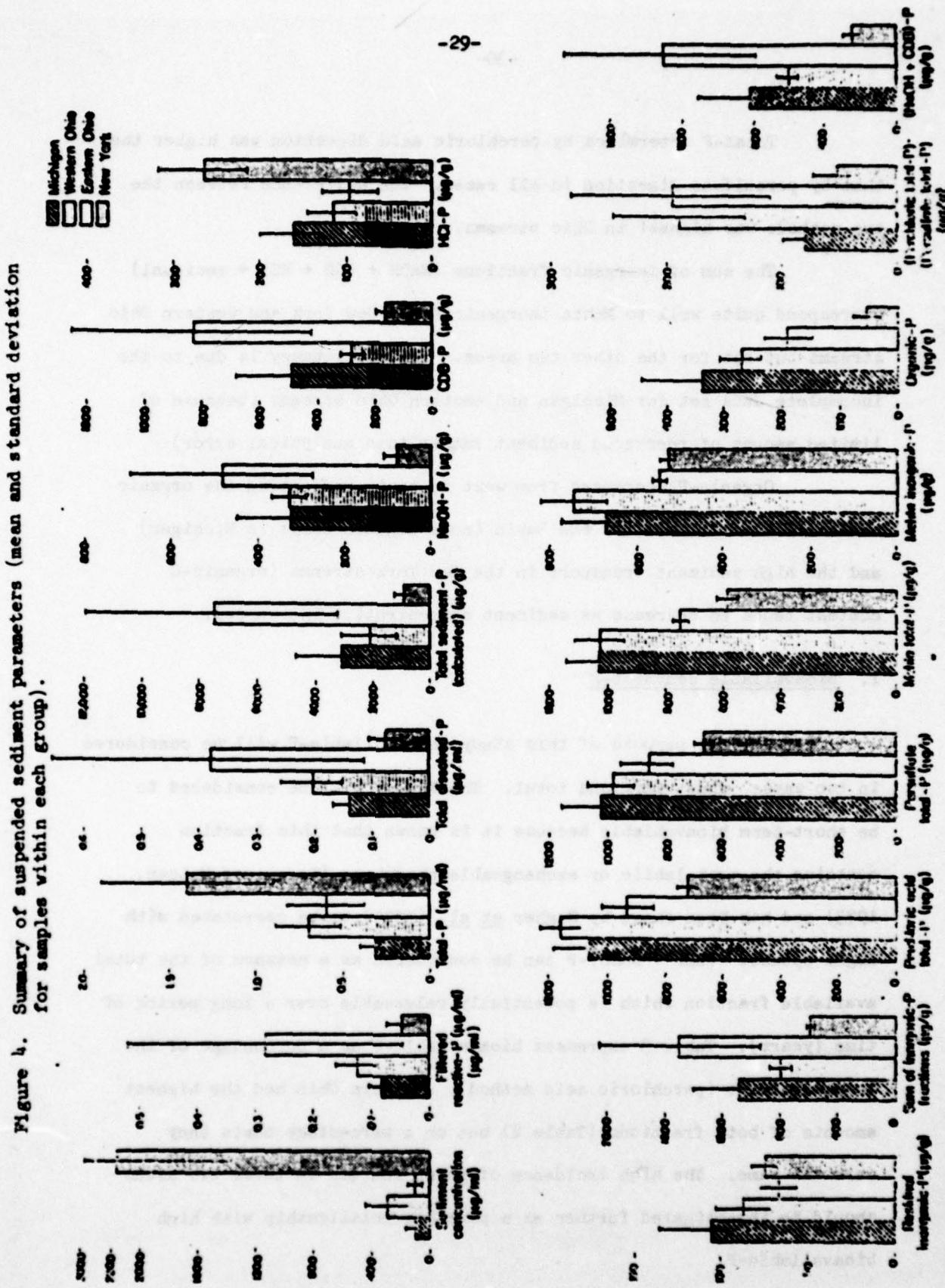
The NaOH-P was essentially the same for Michigan and Ohio streams and these were significantly higher than the New York samples. CDB-P showed the same trend; the eastern Ohio streams had significantly higher values than western Ohio and New York was again lower than the other three areas. On the other hand, HCl-P (apatite) was highest in the New York streams; apatite-P was lowest of three fractions in the Ohio and Michigan streams and highest in the New York tributaries. Sum of the two fractions that are considered to be available (NaOH + CDB) was highest in the eastern Ohio samples, significantly higher than western Ohio and New York. New York was lower than the other three areas.

TABLE 2. SUMMARY OF SEDIMENT-P CHARACTERISTICS

Parameter	No. of Observations	Mean	S.D.	Std. Error of Mean	Minimum	Maximum
Michigan						
Sediment concentration	24	97.5	87.8	17.9	4.0	334.0
Filtered reactive-P	24	0.086	0.043	0.009	0.016	0.151
Total-P	24	0.317	0.170	0.035	0.063	0.606
Total filtered-P	24	0.141	0.054	0.011	0.031	0.276
Total sediment-P	24	3095.0	3168.1	646.7	160.2	15666.7
NaOH-P	24	328.9	238.3	48.7	34.3	2069.4
CDB-P	21	493.7	380.3	83.0	106.2	1614.3
HCl-P	24	162.9	72.2	14.7	40.8	340.6
Residual inorganic-P	21	106.1	58.2	12.7	29.2	245.0
Sum inorganic-P fractions	21	1096.6	603.7	131.7	525.1	2779.7
Perchloric acid total-P	9	1065.5	233.6	77.9	735.0	1477.0
Persulfate total-P	12	1023.5	265.8	76.7	673.2	2524.6
Mehta total-P	11	1032.7	266.2	68.2	668.2	1348.9
Mehta inorganic-P	11	675.0	201.8	60.9	440.6	1118.7
Organic-P	8	341.1	203.3	71.9	96.5	778.4
(Per-Pers)P total-P	9	80.1	37.6	12.5	32.4	126.0
(NaOH+CDB)-P	21	825.3	571.0	124.6	332.2	2408.2
Manatee-Portage-Sandusky-Huron						
Sediment concentration	28	348.8	340.0	64.2	48.0	1204.0
Filtered reactive-P	28	0.123	0.074	0.014	0.025	0.374
Total-P	28	0.706	0.365	0.069	0.234	1.452
Total filtered-P	28	0.201	0.107	0.020	0.082	0.505
Total sediment-P	28	2240.5	2447.0	462.4	901.8	13354.2
NaOH-P	28	330.1	79.2	15.0	121.3	480.8
CDB-P	23	282.4	77.9	16.2	159.3	432.8
HCl-P	28	113.2	64.3	12.1	19.6	261.5
Residual inorganic-P	23	86.1	31.0	6.5	39.2	137.2
Sum inorganic-P fractions	23	787.0	153.6	32.0	503.9	1003.4
Perchloric acid total-P	22	1168.4	136.1	29.0	909.0	1380.4
Persulfate total-P	28	978.4	169.4	32.0	663.3	1287.0
Mehta total-P	26	1029.0	170.8	33.5	705.4	1441.3
Mehta inorganic-P	25	751.8	152.5	30.5	475.2	1211.3
Organic-P	23	270.1	72.7	15.2	173.2	475.2
(Per-Pers)P total-P	21	190.2	115.8	25.3	37.8	430.9
(NaOH+CDB)-P	23	598.9	112.2	23.4	394.9	762.7

Parameter	No. of Observations	Mean	S.D.	Std. Error of Mean	Minimum	Maximum
Eastern Ohio						
Sediment concentration	9	93.6	119.6	39.9	12.0	382.0
Filtered reactive-P	9	0.286	0.492	0.164	0.013	1.485
Total-P	9	0.604	0.518	0.172	0.076	1.749
Total filtered-P	9	0.379	0.555	0.185	0.030	1.768
Total sediment-P	9	7593.0	8613.7	2871.2	1049.5	28555.6
NaOH-P	8	491.5	422.3	149.3	88.6	1332.4
CDB-P	8	834.9	859.3	303.8	181.8	2160.1
HCl-P	8	101.4	61.4	21.7	16.5	180.7
Residual inorganic-P	8	68.5	21.2	7.5	39.2	107.8
Sum inorganic-P fractions	8	1496.2	1134.0	400.9	542.2	3065.6
Perchloric acid total-P	2	934.2	178.5	126.2	808.0	1060.5
Sulfate total-P	3	867.1	224.4	129.5	732.6	1126.1
Mehra total-P	2	742.5	52.5	37.1	705.4	779.6
Mehra inorganic-P	2	551.9	31.5	22.3	529.6	574.2
Organic-P	2	190.6	84.0	59.4	131.2	250.0
(Per-Pers) ^a total P	2	196.7	171.5	121.3	75.4	318.0
(NaOH+CDB)-P	8	1326.4	1090.4	385.5	393.8	2798.3
New York						
Sediment concentration	5	2163.2	1631.1	729.4	292.0	3666.0
Filtered reactive-P	5	0.048	0.051	0.023	0.016	0.136
Total-P	5	1.402	0.985	0.441	0.479	2.95
Total filtered-P	5	0.077	0.053	0.024	0.044	0.170
Total sediment-P	5	973.8	673.2	301.0	309.9	2054.8
NaOH-P	5	83.2	56.4	25.2	36.1	180.1
CDB-P	5	169.9	60.3	27.0	93.9	249.1
HCl-P	5	265.8	29.1	44.3	115.2	357.7
Residual inorganic-P	5	76.4	13.7	6.1	58.8	91.9
Sum inorganic-P fractions	5	595.4	49.2	22.0	546.6	661.3
Perchloric acid total-P	5	720.5	71.0	31.8	664.9	841.6
Sulfate total-P	5	669.2	60.5	27.0	613.8	772.2
Mehra total-P	5	587.2	71.1	31.8	519.8	668.2
Mehra inorganic-P	5	532.6	33.1	14.8	495.0	574.2
Organic-P	5	54.6	41.8	18.7	14.9	104.6
(Per-Pers) ^a total-P	5	51.2	41.2	18.4	1.6	113.0
(NaOH+CDB)-P	5	253.1	103.2	46.2	165.0	179.2

^a Perchloric total-P minus persulfate total-P.



Total-P determined by perchloric acid digestion was higher than that by persulfate digestion in all cases. The difference between the two methods was highest in Ohio streams.

The sum of inorganic fractions (NaOH + CDB + HCl + residual) correspond quite well to Mehta inorganic-P for New York and western Ohio streams but not for the other two areas. The discrepancy is due to the incomplete data set for Michigan and eastern Ohio streams (because of limited amount of recovered sediment rather than analytical error).

Organic-P decreased from west to east, reflecting the organic matter content of soils in the Basin (more organic soils in Michigan) and the high sediment transport in the New York streams (organic-C content tends to decrease as sediment concentration increases).

1. Bioavailable sediment-P

For the purpose of this study, bioavailable-P will be considered in two ways: short-term and total. The NaOH-P will be considered to be short-term bioavailable because it is known that this fraction contains the most labile or exchangeable phosphate (Logan and McLean, 1973) and has been shown by Sagher *et al.* (1975) to be correlated with algal uptake. (CDB + NaOH)-P can be considered as a measure of the total available fraction which is potentially releasable over a long period of time (years). Table 3 expresses bioavailable-P as a percentage of the total sediment (perchloric acid method). Eastern Ohio had the highest amounts of both fractions (Table 2) but on a percentage basis they were the same. The high incidence of point sources in these two areas should be investigated further as a possible relationship with high bioavailable-P.

TABLE 3. PERCENT BIOAVAILABILITY OF SEDIMENT-P*

	NaOH-P	CDB-P	(NaOH + CDB)-P
Michigan	30.0	45.0	75.0
Western Ohio	41.9	35.9	77.8
Eastern Ohio	32.8	55.8	88.6
New York	14.0	28.5	42.5

* Expressed as percent of total sediment inorganic phosphorus.

New York samples were lowest in both NaOH-P and CDB-P and would be expected to support much less algal growth than the streams to the west. On a percentage basis, NaOH-P was lower than other areas. Studies in Fall Creek, New York (Porter, 1975) used a desorption technique to measure readily available phosphorus and concluded that about 4% of the total sediment-P was available by this technique.

Actual bioavailability of sediment-P is strongly dependent on equilibrium kinetics: the rate at which sorbed P is released when a demand or sink (algal uptake) is in operation, and the period during which the sediment is positionally accessible to the algae. In deep lakes with significant stratification, as in the eastern, and to a lesser extent, the central Lake Erie basins, sediment may be in contact with algae for short periods only, during which time NaOH-P will be most important. During anoxia and subsequent lake inversion, P released from the CDB fraction will become significant. Therefore, chemical fractionation data must be interpreted in light of dynamics of the receiving lake.

Simple moment correlations were run between all parameters and Table 4 gives those correlations which were significant at the 5% level of probability or better.^{1/} Sediment concentration was positively correlated with total-P (µg/ml) and HCl-P, and negatively correlated with NaOH-P, total sediment-P and organic-P. A closer examination of the data set (Appendix A) indicates that many of these relationships are reflecting the influence of the New York samples, a number of which were the highest in suspended solids found in the study. The results are, however, supported by the work of Porter (1975), Logan (1978) and Armstrong *et al.* (1977) who found that, at lower sediment concentrations the sediment that is transported contains more clay and organic matter and is higher in sediment-P. Armstrong *et al.* (1977) used a chemical fractionation scheme to characterize suspended sediments from Great Lakes tributaries. They fractionated the sediment into various particle size fractions and showed that available sediment-P was higher on the finer textured material.

Both NaOH-P and CDB-P were correlated with total sediment-P as expected. Step-wise linear regression correlations were run on the various fractions and these are given in Table 5. None of the equations had very high R^2 values. However, a few trends were apparent. CDB-P and (CDB+NaOH)-P were negatively related to sediment concentration, while HCl-P was positively correlated. Total filtered-P was positively correlated with each fraction except CDB-P, and NaOH-P was positively correlated with organic-P. The relationship of this fraction with organic-P is not unexpected since NaOH is known to extract organic

^{1/} Complete correlation matrix is given in Appendix B.

Table 4. Single moment correlation coefficients between sediment-P parameters ^{1/}

	SiO ₂ -P	TiO ₂ -P	TiP	SiO ₂ -P	SiO ₂ -P	TiO ₂ -P	TiP	SiO ₂ -P	SiO ₂ -P	SiO ₂ -P	SiO ₂ -P	
SiO ₂ -P	0.74*	-0.30	0.37*	0.37*	0.15*	0.39	-0.39*	-0.39*	-0.31	-0.39*	-0.31	
TiP	0.31	0.31*	0.39*	-0.28	-0.28	-0.39	-0.39*	-0.39*	-0.37	-0.39	0.17*	
TiO ₂ -P	0.74*	0.31	0.37*	0.36*	0.16*	0.16*	0.16*	0.16*	0.16*	0.16*	0.16*	
TiP	0.34*	0.37	0.36*	0.34*	0.12*	0.17*	0.16*	0.16*	0.16*	0.16*	0.16*	
SiO ₂ -P	-0.30	0.36*	0.36*	0.36*	0.27	0.31*	0.31*	0.31*	0.31*	0.31*	0.31*	
SiO ₂ -P	0.37*	0.39*	0.36*	0.36*	0.37*	0.37*	0.37*	0.37*	0.37*	0.37*	0.37*	
TiO ₂ -P	0.37*	0.38	0.32	0.32	0.27	0.32	0.32	0.32	0.32	0.32	0.32	
SiO ₂ -P	0.45*	0.40*	0.77*	0.91*	0.42*	0.67*	0.83*	0.70*	0.68*	0.70*	0.70*	
SiO ₂ -P	-0.49*	0.39	0.46*	0.46*	0.40	-0.45*	0.42*	0.47*	0.41*	0.43*	0.43*	
TiO ₂ -P	-0.40*	-0.30	0.64*	0.63*	0.51*	0.53*	0.56*	0.53*	0.56*	0.56*	0.56*	
TiO ₂ -P	-0.55*	-0.12*	0.75*	0.84*	0.70*	0.70*	0.81*	0.83*	0.65*	0.65*	0.65*	
SiO ₂ -P	-0.31	0.32	-0.37	0.46*	0.60*	-0.40	0.43*	0.38*	0.61*	0.61*	0.61*	
SiO ₂ -P	-0.52*	0.32	-0.37	0.46*	0.60*	-0.40	0.56*	0.56*	0.65*	0.65*	0.65*	
SiO ₂ -P	0.37	0.39	-0.39	-0.45*	-0.45*	0.45*	0.45*	0.45*	0.45*	0.45*	0.45*	
CIN	0.31	0.47	0.41*	0.79*	0.91*	0.36*	0.99*	0.83*	0.82*	0.79*	0.70*	0.18*

^{1/} All coefficients given are significant at the 5% level or better. Those with "*" are significant at the 1% level.

^{2/} SiO₂-P = $\text{SiO}_2 \text{-P}$ (SiO₂-P) - $\text{P}_{\text{resid}} \text{-P}$ (SiO₂-P)

^{3/} SiO₂-P + TiO₂-P = $\text{SiO}_2 \text{-P} + \text{TiO}_2 \text{-P}$ (SiO₂-P + TiO₂-P) - $\text{P}_{\text{resid}} \text{-P}$ (SiO₂-P + TiO₂-P)

material; although only the inorganic-P in the NaOH extract was measured, it is possible that the NaOH may be extracting a part of the inorganic-P that is bound to organic matter or there may be extraction of polyphosphates with subsequent hydrolysis to inorganic reactive-P.

TABLE 5. STEPWISE LINEAR REGRESSION EQUATIONS

$$\text{NaOH-P} = 333.1 \text{ total filtered-P} + 0.26 \text{ organic-P} - 0.60 \text{ HCl-P} + 217.3 \quad R^2 = 0.57$$

$$\text{CDB-P} = 1.52 \text{ residual inorganic-P} - 0.04 \text{ sediment conc.} + 169.2 \quad R^2 = 0.39$$

$$\begin{aligned} \text{HCl-P} = & 0.03 \text{ sediment concentration} + 162.9 \text{ filtered reactive-P} + 205.8 \text{ total filtered-P} - 0.30 \\ & \text{NaOH-P} - 0.23 \text{ (Perchloric acid total-P-} \\ & \text{persulfate acid total-P)} + 182.2 \end{aligned} \quad R^2 = 0.56$$

$$\begin{aligned} (\text{NaOH+CDB})-\text{P} = & 600.7 \text{ total filtered-P} + 2.03 \text{ residual inorganic-P} - 0.06 \text{ sediment concentration} - 0.57 \text{ HCl-P} + 373.4 \end{aligned} \quad R^2 = 0.63$$

2. Total Sediment-P Analysis

One of the objectives of this study was to compare the persulfate method of total-P analysis with perchloric acid digestion used in soil analysis. O'Connor and Syers (1975) showed that when water samples contain significant amounts of mineral sediment, persulfate digestion fails to recover all of the P present. They attributed the difference between persulfate and the more rigorous perchloric acid digestion to highly resistant inorganic-P forms.

Our data (Table 2) showed that perchloric acid does extract more P than persulfate in all cases. The difference in sediment-P extracted was positively correlated with total filtered-P and negatively correlated with HCl-P. Step-wise linear regression gave the following equation:

$$\text{Difference in total-P} = 517.9 \text{ total filtered-P} - 0.38 \text{ CDB-P} - 0.67 \text{ HCl-P} + 258.2 \quad R^2 = 0.42$$

The R^2 was quite low but confirmed the negative correlation with HCl-P. Evidently the perchloric acid is extracting some form of P in the samples from Ohio and Michigan not seen in the New York samples and that this form is not organic-P or residual inorganic-P since these did not correlate.

3. Extrapolation to Lake Erie

Monitored tributary loads of sediment to Lake Erie in recent years have shown that most of the sediment is transported during storm events. These sediments are primarily of surficial soil origin, with detrital sediment and street litter from urban runoff of lesser significance. PLUARG - Task C studies in the Menominee River Basin and work by Cowen and Lee (1976) in New York and Wisconsin indicate that urban sediments have phosphorus characteristics similar to those from agricultural areas.

Sediment-P bioavailability as measured by chemical extraction, bioassay or other techniques reflects, for the most part, native soil phosphorus levels in Basin soils and its chemical and biological reactivity, fertilizer phosphorus additions, the degree to which sediment is enriched in P because of preferential clay transport, and the adsorption of point source soluble inorganic P by stream sediments.

Based on these considerations, sediments from the more urbanized tributary areas in Michigan and eastern Ohio and those from the high clay agricultural basins in western Ohio should have the highest BSP per unit sediment load. The high total annual sediment load in the Maumee, Portage and Sandusky basins together with high BSP point to these areas as the major contributors of BSP. In addition, the discharge of these sediments into the shallow western basin of Lake Erie make their impact on algal production even more significant. As one proceeds into the central and eastern basins, the significant contribution of sediment-P to algal growth is diminished for two reasons: lower sediment loads and BSP, and shorter contact time between algae and sediment.

Reductions in total sediment load to the Lake in concert with point source phosphorus reductions have been proposed. Sediment load reductions in the NW Ohio region of the Lake basin should receive greatest attention. In this regard, two points should be made: 1) While total fertilizer P additions since modern chemical fertilization began about 40 years ago have only increased soil-P levels by about 10%, these additions have a higher BSP than native soil-P. Logan (1978) found that Lake Erie Basin agricultural soils had available-P levels sufficient for optimum crop production and state extension programs should strive to maintain these levels rather than increase them further. 2) sediment-P reductions will not be as great as sediment reduction when conservation programs are implemented, because these programs are more efficient at preventing the loss of coarse-grained sediment than the fine sediment with its higher P content. The results of Armstrong *et al.* (1977) indicate that BGP will also diminish slower than sediment reduction.

CONCLUSIONS

1. Bioavailable sediment-P as estimated by NaOH extraction was on the order of 30-40% of total inorganic sediment-P for suspended sediments in Michigan and Ohio. New York sediments were only half as much, about 14%.
2. New York sediments had the highest content of apatite-P and were lowest in total-P.
3. Persulfate gave lower total sediment-P values than perchloric acid in all cases; this difference was negatively correlated with apatite-P but was not correlated with organic-P or residual inorganic-P.

REFERENCES

1. Allan, R. J. and J.D.H. Williams. 1978. Trophic status related to sediment chemistry of Canadian Prairie Lakes. *Jour. Envir. Qual.* 7(1)99-106.
2. Amer, F., D. R. Bouldin, C. A. Black and F. R. Luke. 1955. Characterization of soil phosphorus by anion exchange resin adsorption and P₃₂ equilibration. *Plant Soil* 6:391-408.
3. Armstrong, D. E., M. A. Anderson, J. R. Perry, and D. Flatness. 1977. Availability of pollutants associated with access to the Great Lakes. Unpublished. EPA Progress Report. Wisconsin.
4. Bache, B. W. 1963. Aluminum and iron phosphate studies relating to soils: 1. *Jour. Soil Sci.* 14:113-123.
5. Bache, B. W. 1964. Aluminum and iron phosphate studies relating to soils: 2. *Jour. Soil Sci.* 15:110-116.
6. Baum, G. R. and E. H. Tyner. 1957. The nature of reductant soluble phosphorus in soils and soil concretions. *Soil Sci. Soc. Amer. Proc.* 21:250-257.
7. Bray, R. H. and L. T. Kurtz. 1945. Determination of total, organic, and available forms of phosphorus in soils. *Soil Sci.* 59:39-45.
8. Chang, S. C. and M. L. Jackson. 1957. Fractionation of soil phosphorus. *Soil Sci.* 84:133-144.
9. Cowen, W. F. and G. F. Lee. 1976. Algal nutrient availability and limitation in Lake Ontario tributary waters. *Ecological Research Series.* EPA-600/3-76-094a.
10. Fiskell, J.G.A. and W. R. Spencer. 1964. Forms of phosphate in Lakeland fine sand after six years of heavy phosphate and lime applications. *Soil Sci.* 97:320-325.
11. Golterman, H. L. 1976. Sediments as a source of phosphorus for algae growth. In H. L. Golterman (Ed.). *Interactions between sediments and freshwater.* Proc. 5LL-UNESCO Conf. Junk and Pudoc, The Hague, Netherlands.
12. Golterman, H. L. 1977. Forms and sediment associations of nutrients, pesticides and metals. *Nutrients-P.* In Proc. Workshop on Fluvial Transport of Sediment-associated nutrients and contaminants. H. Shear, Ed. IJC-PLUARG, Windsor, Ontario.

13. Green, D. B., T. J. Logan and N. E. Smeck. 1978. Phosphate adsorption-desorption characteristics of suspended sediments in the Maumee River Basin of Ohio. *Jour. Envir. Qual.* 7:208-212.
14. John, M. K. 1970. Colorimetric determination of phosphorus in soil and plant materials with ascorbic acid. *Soil Sci.* 109:214-220.
15. Li, W. C., D. E. Armstrong, J.D.H. Williams, R. F. Harris and J. K. Syers. 1972. Rate and extent of inorganic phosphorus exchange in lake sediments. *Soil Sci. Soc. Amer. Proc.* 36:279-285.
16. Logan, T. J. and E. O. McLean. 1973. Nature of phosphorus retention and adsorption with depth in soil columns. *Soil Sci. Soc. Amer. Proc.* 37:351-355.
17. Logan, T. J. 1978. Available phosphorus levels in Lake Erie Basin soils. *LEWMS Final Technical Reports.* Corps of Engineers, Buffalo District, Buffalo, N.Y.
18. Logan, T. J. 1978. Maumee River Basin pilot watershed study. *PLUARG Task C. Summary Technical Report.* IJC, Windsor, Ont.
19. McCallister, D. L. and T. J. Logan. 1978. Phosphate adsorption-desorption characteristics of soils and bottom sediments in the Maumee River Basin of Ohio. *Jour. Envir. Qual.* 7:87-92.
20. Mehta, N. C., J. O. Legg, C.A.I. Goring and C. A. Black. 1954. Determination of organic phosphorus in soils. 1. Extraction method. *Soil Sci. Soc. Amer. Proc.* 18:443-449.
21. Murphy, J. and J. P. Riley. 1962. A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta.* 27:31-36.
22. Nelson, D. W. 1977. Algal studies. In: *Environmental impact of land use on water quality.* EPA Tech. Rep. Page 221.
23. O'Connor, P. W. and J. K. Syers. 1975. Comparison of methods for the determination of total phosphorus in water containing particulate material. *J. Envir. Qual.* 4:347-350.
24. Olsen, S. R., C. V. Cole, F. Watanabe and L. A. Dean. 1954. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. *USDA Circular 939.*
25. Patrick, W. H. and I. C. Mahapatra. 1968. Transformation and availability of nitrogen and phosphorus in waterlogged soils. *Advan. Agron.* 20:323-359.
26. Porter, K. S. 1975. *Nitrogen and phosphorus, food production, waste and the environment.* Ann Arbor Science, Ann Arbor, Mich. 372 pages.

27. Rajan, S.S.S. and R. L. Fox. 1975. Phosphate sorption by soils: II. Reactions in tropical acid soils. *Soil Sci. Soc. Amer. Proc.* 39:846-851.
28. Reddy, G. Y., E. O. McLean, G. D. Hoyt and T. J. Logan. 1978. Effects of soil, cover crop, and nutrient source on amounts and forms of phosphorus movement under simulated rainfall conditions. *Jour. Envir. Qual.* 7:50-54.
29. Robertson, W. K., L. G. Thompson, Jr. and C. E. Hutton. 1966. Availability and fractionation of residual P in soils high in aluminum and iron. *Soil Sci. Soc. Amer. Proc.* 30:446-451.
30. Romkens, M.J.M. and D. W. Nelson. 1974. Phosphorus relationships in runoff from fertilized fields. *Jour. Envir. Qual.* 3:10-14.
31. Ryden, J. C., J. K. Syers and R. F. Harris. 1972. Potential of an eroding urban soil for the phosphorus enrichment of streams: Evaluation of methods. *Jour. Envir. Qual.* 1:420-434.
32. Ryden, J. C., J. R. McLaughlin and J. K. Syers. 1977. Time-defendent sorption of phosphate by soils and hydrous ferric oxides. *Jour. Soil Sci.* 28:585-595.
33. Sagher, A., R. F. Harris, and D. E. Armstrong. 1975. Availability of sediment phosphorus to microorganisms. *Univ. of Wisconsin Water Res. Cent. Tech. Report WIC WRC 75-01. Wisconsin.*
34. Sommers, L. E. and D. W. Nelson. 1972. Determination of total phosphorus in soils: A rapid perchloric acid digestion procedure. *Soil Sci. Soc. Amer. Proc.* 36:902-904.
35. Standard methods for the examination of water and wastewater. 13th Edition. 1971. American Public Health Assoc. Washington, D.C. Page 526.
36. Syers, J. K., G. W. Smillie and J.D.H. Williams. 1972. Calcium fluoride formation during extraction of calcareous soils with fluoride I. Implication to inorganic P fractionation schemes. *Soil Sci. Soc. Amer. Proc.* 36:20-25.
37. Taylor, A. W. and H. M. Kunishi. 1971. Phosphate equilibria on stream sediment and soil in a watershed draining an agricultural region. *Jour. Agr. Food Chem.* 19:827-831.
38. Weaver, R. M. 1974. A simplified determination of reductant-soluble phosphate in soil phosphate fractionation schemes. *Soil Sci. Soc. Amer. Proc.* 38:153-154.

39. Williams, J.D.H., T. P. Murphy, and T. Mayer. 1976. Rates of accumulation of phosphorus forms in Lake Erie sediments. *J. Fish. Res. Board Can.* 33:430-439.
40. Williams, J.D.H., J. K. Syers, and T. W. Walker. 1967. Fractionation of soil inorganic phosphate by a modification of Chang and Jackson's procedure. *Soil Sci. Soc. Amer. Proc.* 31:736-739.
41. Williams, J.D.H., J. K. Syers, R. F. Harris, and D. E. Armstrong. 1971a. Fractionation of inorganic phosphate in calcareous lake sediments. *Soil Sci. Soc. Amer. Proc.* 35:250-255.
42. Williams, J.D.H., J. K. Syers, D. E. Armstrong, and R. F. Harris. 1971b. Characterization of inorganic phosphate in noncalcareous lake sediments. *Soil Sci. Soc. Amer. Proc.* 35:556-561.
43. Williams, J.D.H. and T. W. Walker. 1969. Fractionation of phosphate in a maturity sequence of New Zealand basaltic soil profiles: 1. *Soil Sci.* 107:22-30.
44. Williams, J.D.H. and T. W. Walker. 1969. Fractionation of phosphate in a maturity sequence of New Zealand basaltic soil profiles: 2. *Soil Sci.* 107:213-219.

APPENDIX

DAYS	DATE	SITE	TFP		TFTR	
			SEDCON	TFPP	SEDCON	TFTRP
1	NOV 5	BELLE	143	0.249	0.196	0.177
2	NOV 5	BLACK	376	0.113	0.496	0.115
3	NOV 5	CLIVTON	214	0.116	0.115	0.209
4	NOV 5	MURKIN	16	0.146	0.164	0.132
5	NOV 5	MILL CREEK	68	0.141	0.385	0.146
6	NOV 5	RAISIN	234	0.114	0.606	0.177
7	NOV 5	REFUGE	142	0.141	0.330	0.279
8	NOV 5	SASPARA	156	0.112	0.113	0.029
9	NOV 5	SELL	58	0.144	0.240	0.107
10	NOV 5	BLACK	146	0.146	0.406	0.132
11	NOV 5	CLIVTON	133	0.044	0.340	0.114
12	NOV 5	MURKIN	26	0.062	0.177	0.092
13	NOV 5	MILL CREEK	46	0.075	0.252	0.152
14	NOV 5	RAISIN	334	0.046	0.549	0.193
15	NOV 5	ROUGE	126	0.153	0.391	0.213
16	NOV 5	SASHABAW	12	0.335	0.107	0.089
17	NOV 5	BELLE	6	0.283	0.196	0.101
18	NOV 5	BLACK	10	0.132	0.145	0.123
19	NOV 5	CLIVTON	52	0.175	0.372	0.132
20	NOV 5	MURKIN	10	0.026	0.124	0.107
21	NOV 5	MILL CREEK	4	0.084	0.150	0.125
22	NOV 5	RAISIN	112	0.282	0.303	0.103
23	NOV 5	ROUGE	80	0.131	0.434	0.138
24	NOV 5	SASHABAW	4	0.016	0.063	0.031
25	NOV 5	ANGLAISE	21	0.133	0.234	0.164

-43-

RESIP	PRAIP	PACTP	PASTP	WATP	WAIWP	CRCP	DIFFP	LOC	SUM	PER14	PERTA
1	83.3	863.9	1212.0	1173.1	1293.2	514.9	778.4	33.0	701.0	0.356923	0.578383
2	93.9	614.5	1009.8	920.7	1076.6	702.4	373.7	25.1	426.9	0.235633	0.426427
3	53.3	767.1	1077.2	950.4	1107.6	772.2	335.4	126.9	483.5	0.247958	0.448849
4	137.2	682.6	-	-	801.9	773.4	732.6	-	492.3	-	-
5	69.6	980.9	1287.0	1356.3	1249.4	440.6	-	120.7	-	0.344617	0.519102
6	72.5	956.9	625.6	903.2	900.9	1072.4	693.0	377.4	92.3	0.246596	0.516596
7	52.4	525.1	34.3	735.0	613.2	660.2	540.0	349.0	61.3	0.1451975	0.451975
8	29.2	862.7	-	-	-	-	-	-	472.9	-	-
9	149.4	1205.5	-	-	-	-	-	-	926.6	-	-
10	63.3	740.1	791.2	742.5	742.5	-	-	-	511.1	0.109201	0.645981
11	91.9	92.1	707.7	-	-	-	-	-	441.9	-	-
12	131.0	993.1	-	-	-	-	-	-	799.6	-	-
13	261.0	2779.7	-	-	-	-	-	-	2408.2	-	-
14	159.5	2622.7	-	-	-	-	-	-	2275.2	-	-
15	117.6	919.9	-	-	1243.2	-	-	-	547.1	-	-
16	139.1	1599.3	-	-	-	-	-	-	1195.8	-	-
17	99.1	1575.1	-	-	-	-	-	-	1445.2	-	-
18	226.4	2019.0	-	-	821.7	977.1	-	-	949.6	-	-
19	117.6	2024.4	-	-	1524.6	1345.7	-	-	860.4	-	-
20	139.1	230.2	93.0	93.0	-	-	-	-	687.2	-	-
21	99.1	1137.2	-	-	-	-	-	-	394.9	0.130542	0.424986
22	86.2	1024.4	-	-	-	-	-	-	226.3	-	-
23	93.0	929.2	702.9	702.9	-	-	-	-	220.0	-	-
24	245.0	230.2	93.0	93.0	-	-	-	-	220.0	-	-

APPENDIX A Continued

SUMMARY OF DATA OF INDIVIDUAL SITES										14:35 WEDNESDAY, AUGUST 23, 1978				24	
DS	DATE	SITE	SECON	F ₄₀	TF ₁₀	TF ₀	TF ₋₁₀	TF ₋₄₀	WADIP	CDFP	MCDFP	LOC	LOC	PERIA	PERIA
21	JULY 5	WAUNEE/WATERVILLE	158	0.103	0.335	0.102	1436.7	266.0	432.8	132.3					
32	JULY 21	SANDUSKY/BUCYRUS	420	0.215	1.054	0.404	2419.0	427.5	310.3	76.0					
32	JUNE 4	RIC CREEK	19	0.149	0.327	0.223	5222.2	880.4	1911.0	132.3					
34	JUNE 6	CHAGRIN RIVER	394	0.016	0.492	0.101	1049.5	195.1	148.7	180.7					
35	JUNE 8	CUYAHOGA	52	0.610	0.928	0.657	740.0	1332.4	1665.9	179.3					
36	JUNE 6	WOODKINS CREEK	46	0.056	0.152	0.063	1934.8	966.8	343.0	34.9					
37	JUNE 6	NEFF RUN	38	0.013	0.555	0.177	12263.2	275.0	212.3	16.5					
38	JUNE 6	MONAVILLE DITCH	78	0.010	0.854	0.313	6359.0	375.4	206.2	63.7					
39	JUNE 6	GRAY CREEK	172	0.074	0.303	0.076	1392.0	222.2	191.3	99.2					
40	JUNE 6	ROCKY RIVER	36	1.435	1.749	1.769	20555.6	85.6	2160.1	104.1					
41	JULY 7	MUARA-C-KUN	12	0.020	0.076	0.030	4166.7								
42	JULY 28	CATTARAUGUS	3602	0.138	2.954	0.172	772.9	711.1	93.9	350.7					
43	APR 23	CATTARAUGUS	3666	0.016	1.199	0.064	304.9	30.1	175.6	357.7					
44	APR 23	DELAWARE	292	0.264	0.479	0.050	2054.8	189.1	249.1	119.2					
45	APR 23	EIGHTIETH MI CREEK	2696	0.029	1.655	0.059	501.6	52.7	200.1	234.5					
46	APR 23	SOUTH CATTARAUGUS	370	0.032	0.694	0.050	1129.3	76.0	130.7	271.3					
47	RESIP	PACTP	PRSTP	WADIP	WADIP	CRCP	CRCP	DIFFP	LOC	LOC	LOC	LOC	LOC	PERIA	PERIA
21	93.0	929.1	1175.4	1059.3	1113.9	841.5	272.3	119.1	2	698.8	0.2225730	0.593007			
32	137.2	951.3	1296.2	1163.2	705.4	-	-	-	2	739.1	0.2330042	0.589434			
32	78.4	3002.1	-	-	-	-	-	-	3	2791.4	-				
34	58.8	633.3	800.0	732.6	705.4	574.2	131.2	75.4	3	393.8	0.2414460	0.437376			
35	107.8	3082.6	-	-	-	-	-	-	3	2798.3	-				
36	69.0	1013.3	-	-	-	-	-	-	3	609.8	-				
37	52.1	553.9	-	-	-	-	-	-	3	685.3	-				
38	33.3	726.6	-	-	1126.1	-	-	-	3	579.6	-				
39	39.2	542.2	1069.3	742.5	779.6	529.6	250.0	319.0	3	406.0	0.209524	0.380952			
40	60.0	2612.8	-	-	-	-	-	-	3	2248.7	-				
41	58.0	-	-	974.2	690.2	643.5	555.9	536.6	22.3	46.7	165.0	0.103014	0.239061		
41	91.9	661.3	664.9	663.3	516.9	504.9	14.9	1.6	211.7	0.054244	0.319339				
42	59.2	632.6	341.6	772.2	643.2	574.2	94.0	69.4	429.2	0.213997	0.539991				
43	74.7	562.1	681.5	653.4	532.1	495.0	37.1	25.4	252.3	0.077295	0.307793				
44	68.6	546.6	723.8	613.8	659.0	554.4	104.6	110.0	206.7	0.105301	0.255576				

-45-

APPENDIX B

STATISTICAL ANALYSIS SYSTEM 14:35 WEDNESDAY, AUGUST 23, 1972

CORRELATION COEFFICIENTS / PQRS > 191 UNDER M01N00 / NUMBER OF OBSERVATIONS

SECON	FREQ	T010	T010	T5EDP	YATMP	CDBP	HC1P	RES1P	FRA1P	PRCTP	PRSTP	WHTP
SECON	1.00000	-0.110235	0.742233	-0.092222	-0.230552	-0.301555	-0.25342	0.267770	-0.11453	-0.25832	-0.49284	-0.4378
FREQ	0.20000	-0.41449	0.05021	0.4615	0.0621	0.3143	0.0572	0.0026	0.2703	0.0524	0.0017	0.0004
FREQ	0.40000	-0.122025	0.31163	0.93974	0.66097	0.79137	0.59493	-0.02769	-0.07313	0.44560	0.39220	0.25818
T010	0.742259	0.31163	1.00000	0.36296	0.12771	-0.20557	-0.07150	0.12219	-0.28544	-0.14144	-0.27270	-0.30154
T010	-0.092222	0.95974	0.36796	1.00000	0.64704	0.57729	0.34039	-0.09359	-0.10194	0.40457	0.44400	0.23463
HC1P	-0.235555	0.66097	0.12771	0.64709	1.00000	0.22118	0.59153	-0.16503	0.15936	0.49275	0.17975	0.11714
HC1P	0.0625	0.0001	0.30683	0.0001	0.0000	0.0766	0.0001	0.1195	0.2364	0.0001	0.2802	0.42770
RES1P	-0.302255	0.00137	-0.20657	0.07029	0.22118	1.00000	0.54153	-0.18805	0.41922	0.77022	0.86364	0.64391
RES1P	0.0143	0.4644	0.0001	0.5997	0.5779	0.0766	0.0001	0.1936	0.0012	0.0001	0.0001	0.0001
CDBP	-0.25342	0.59493	-0.07150	0.56019	0.59153	0.54153	1.00000	0.01553	0.27003	0.93777	0.39698	0.69623
CDBP	0.0572	0.0001	0.5971	0.0001	0.0001	0.0766	0.0001	0.9077	0.3422	0.0001	0.0192	0.0001
YATMP	0.367773	-0.32763	0.12219	-0.03598	-0.19503	-0.18904	0.01553	1.00000	-0.04923	0.06778	-0.44859	-0.31101
YATMP	0.0025	0.2267	0.33212	0.5080	0.1165	0.1336	0.0087	0.0000	0.7161	0.6164	0.0047	0.5608
FRA1P	-0.16234	-0.07213	-0.28544	-0.10195	0.15935	0.41922	0.27003	-0.04923	1.00000	0.41633	0.41834	0.50986
FRA1P	0.0017	0.46860	-0.16144	0.43657	0.49275	0.77222	0.93777	0.04779	0.41633	1.00000	0.67336	0.93275
PRCTP	-0.40372	0.25615	-0.30154	0.23463	0.11714	0.54391	0.67623	-0.01131	0.50366	0.93275	0.24665	1.30000
PRCTP	0.0017	0.5149	0.0976	0.0033	0.2202	0.0001	0.0192	0.0001	0.0125	0.0001	0.0001	0.0001
PRSTP	-0.40372	0.25615	-0.30154	0.23463	0.11714	0.54391	0.67623	-0.01131	0.50366	0.93275	0.24665	1.30000

APPENDIX B Continued
 STATISTICAL ANALYSIS SYSTEM
 14:35 WEDNESDAY, AUGUST 23, 1978

CORRELATION COEFFICIENTS / PRED > INI UNDER MODE=0 / NUMBER OF OBSERVATIONS													
SEDCN	FRP	TOTP	TFP	TSED	NICNP	COBP	HCLP	RESIP	FRAIP	PCCTP	PASTP	WATP	
WATP	-0.35168 0.6001	0.13932 0.3694	-0.41693 0.0049	0.20549 0.1734	0.23242 0.1281	0.71442 0.0031	0.49417 0.0016	-0.16310 0.2901	0.21351 0.1814	0.69643 0.0001	0.82636 0.3051	1.00000 0.0001	
WATP	-0.30655 0.0435	0.02571 0.3700	-0.22672 0.1437	0.046157 0.7913	0.16055 0.3034	0.37513 0.6124	0.60523 0.0001	-0.10261 0.5126	0.446704 0.0031	0.68556 0.0001	0.57806 0.3078	0.644837 0.001	
WATP	-0.52445 0.0007	0.31444 0.0506	-0.37431 0.0205	0.46652 0.0033	0.22969 0.1654	0.56704 0.0001	0.09756 0.5714	-0.39669 0.0137	0.29561 0.9750	0.29496 0.0802	0.45580 0.0006	0.66719 0.0001	
PCCTP	-0.17891 0.2569	0.08050 0.6358	0.02172 0.5995	0.37245 0.0163	0.04945 0.7713	0.30412 0.6472	0.30412 0.5291	-0.11179 0.0051	-0.11600 0.5136	-0.05944 0.7386	0.45161 0.0050	-0.04720 0.7814	0.13970 0.4096
PCCTP	0.52291 0.6001	0.14420 0.2480	0.51675 0.3031	0.13471 0.2804	0.07807 0.5332	0.05837 0.4924	0.03127 0.8174	-0.05912 0.4852	-0.29696 0.0304	-0.06752 0.6177	-0.51065 0.0011	-0.45213 0.0013	-0.57911 0.0001
SUM	-0.30925 0.0197	0.46370 0.0002	-0.14093 0.29513	0.43646 0.0007	0.52277 0.0001	0.79073 0.0001	0.94286 0.0001	-0.07051 0.6022	0.36281 0.0055	0.98810 0.0001	0.82897 0.0001	0.78497 0.0001	
PERMA	-0.49536 0.0016	0.28745 0.0801	-0.19351 0.2434	0.42088 0.0083	0.25066 0.0001	0.95105 0.1200	0.14431 0.4092	-0.51860 0.0009	0.66512 0.7101	0.51565 0.0015	0.70445 0.0001	0.69560 0.0001	
PERTA	-0.55605 0.0006	0.16991 0.3294	-0.353107 0.0212	0.346815 0.0404	0.16963 0.3307	0.55331 0.0006	0.75575 0.0001	-0.41047 0.0143	0.21097 0.2238	0.67608 0.0001	0.39641 0.0164	0.50003 0.0022	0.47652 0.0018
SEDCDN	-0.33693 0.0036	-0.52444 0.0007	-0.17691 0.2969	0.52951 0.0001	-0.30825 0.0197	-0.49504 0.0016	-0.30825 0.0197	-0.49504 0.0016	-0.30825 0.0197	-0.49504 0.0016	-0.30825 0.0197	-0.49504 0.0016	
FRP	0.02571 0.8700	0.31944 0.0506	0.08053 0.6358	0.14420 0.2480	0.46670 0.0002	0.21745 0.0002							
TFP	-0.22072 0.1437	-0.37431 0.0206	0.32172 0.3935	0.51675 0.0001	-0.14090 0.2953	-0.19371 0.27434							
TFP	0.34157 0.7913	0.46442 0.0033	0.39245 0.0163	0.13471 0.2804	0.43646 0.0001	0.42098 0.0001							

DISCUSSIONS OF THE INFLUENCE OF THE ENVIRONMENT ON THE
MIGRATION OF THE BROWN SPARROW

卷之三

PERTA	PERNA	SU4	SU1	LCF	CFP	CRGP	MAP	MAP	PERTA
0.16065 0.33344	0.22959 0.16544	0.04945 0.77113	0.07507 0.53332	0.52277 0.00611	0.20066 0.12900	0.16663 0.33000	0.16065 0.33344	0.16065 0.33344	0.16065 0.33344
0.37813 0.00953	0.59966 0.09756	0.30412 -0.11179	-0.78867 -0.03127	0.79073 0.94294	0.35105 0.14431	0.95351 0.79355	0.00066 0.40392	0.00066 0.40392	0.00066 0.40392
0.01244 0.00701	0.30031 0.57114	0.05722 0.32291	0.48224 0.31740	0.00011 0.00011	0.00011 0.40392	0.00011 0.70010	0.37 35	0.37 35	0.37 35
0.10261 0.51200	-0.39640 0.31377	-0.45071 0.00511	0.08812 0.48552	-0.07051 0.60221	-0.51860 0.00015	-0.41267 0.21097	0.40392 0.71010	0.40392 0.22329	0.40392 0.22329
0.46704 0.02331	-0.00541 0.97500	-0.11600 0.52136	-0.28696 0.03040	0.36221 0.00015	0.06512 0.71010	0.21097 0.22329	0.40392 0.35	0.40392 0.35	0.40392 0.35
0.08556 0.00011	0.29496 0.05014	-0.05644 0.73934	-0.06752 0.61777	0.08818 0.00011	0.51965 0.00115	0.67609 0.00011	0.40392 0.35	0.40392 0.35	0.40392 0.35
0.43077 0.00078	0.55573 0.00006	0.49161 0.00510	-0.51065 0.00111	0.82897 0.00011	0.70649 0.00011	0.39644 0.01960	0.40392 0.35	0.40392 0.35	0.40392 0.35
0.57836 0.00511	0.45580 0.05464	-0.06720 0.78114	-0.45213 0.00113	0.82360 0.00113	0.682440 0.00011	0.50003 0.00022	0.40392 0.35	0.40392 0.35	0.40392 0.35
0.646637 0.00001	0.64713 0.00011	0.13970 0.40961	-0.57911 0.00011	0.73957 0.00011	0.69567 0.00011	0.47652 0.00011	0.42171 0.04920	0.42171 0.04920	0.42171 0.04920
1.00000 0.59220	0.10713 0.30000	0.06167 0.36900	-0.26588 0.62108	0.70294 0.00029	0.32705 0.00029	0.42171 0.00044	0.22460 0.00044	0.22460 0.00044	0.22460 0.00044
0.000167 0.000167	0.15903 0.3690	1.00000 0.00000	-0.06770 0.69095	0.21139 0.23011	0.22469 0.16240	0.08936 0.61530	0.10000 0.66661	0.10000 0.66661	0.10000 0.66661
0.71649 0.000167	0.71649 0.3690	0.00000 0.69095	-0.06770 1.00000	0.21139 -0.062115	0.22469 0.16240	0.08936 0.61530	0.42171 0.10000	0.42171 0.10000	0.42171 0.10000
0.000167 0.000167	0.62105 0.000167	-0.62105 0.69095	0.06770 1.00000	0.21139 -0.062115	0.22469 0.16240	0.08936 0.61530	0.42171 0.10000	0.42171 0.10000	0.42171 0.10000

APPENDIX B Continued
STATISTICAL ANALYSIS SYSTEM

14:35 WEDNESDAY, AUGUST 23, 1978

CORRELATION COEFFICIENTS / PROB. > 1 RI UNDER MORNHOE / NUMBER OF OBSERVATIONS

SNALP	ORGP	DIFFP	LOC	SUN	PIRMA	PERTA
SUN	0.70594 0.0001	0.49235 0.0029	0.21139 0.7301	-0.06215 0.6461	1.00000 0.0000	0.76927 0.0001
	38	36	34	57	47	35
PIRMA	0.32706 0.0042	0.57736 0.0054	0.233643 0.1524	-0.42564 0.0077	0.76227 0.0001	1.00000 0.0000
	37	34	37	38	35	38
PERTA	0.42171 0.0052	0.32460 0.0653	-0.02936 0.6153	-0.53536 0.0009	0.92731 0.0001	0.60000 0.0001
	34	33	34	35	35	35